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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 4 :</b> <b>A61L 15/07</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 88/ 02636</b> <b>(43) International Publication Date:</b> 21 April 1988 (21.04.88)
<b>(21) International Application Number:</b> PCT/GB87/00716 <b>(22) International Filing Date:</b> 13 October 1987 (13.10.87) <b>(31) Priority Application Number:</b> 8624645 <b>(32) Priority Date:</b> 14 October 1986 (14.10.86) <b>(33) Priority Country:</b> GB  <b>(71) Applicant (for all designated States except US):</b> SMITH AND NEPHEW ASSOCIATED COMPANIES PLC [GB/GB]; 2 Temple Place, Victoria Embankment, London WC2R 3BP (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> HICKS, John, Kenneth [GB/GB]; 92 Boulevard, Hull, North Humberside (GB). FRY, Nicholas, Charlton [GB/GB]; 572 Hotham Road South, Hull, North Humberside (GB).		<b>(74) Agent:</b> COLE, W., G.; Smith & Nephew Research Limited, Gilston Park, Harlow, Essex CM20 2RQ (GB).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> BANDAGES  <b>(57) Abstract</b>  Water hardenable splinting bandages comprising a flexible fabric carrying a water curable isocyanate terminated prepolymer and a catalyst therefor wherein the prepolymer is in admixture with an organic acid anhydride to inhibit premature setting of the bandage on storage, water curable isocyanate terminated prepolymers and water hardenable compositions for use in the bandages and methods for their preparation.		

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BANDAGES

The present invention relates to a water hardenable, polyurethane orthopaedic splinting bandage comprising a flexible fabric supporting a water curable isocyanate terminated prepolymer, a catalyst for the curing reaction and additive which stabilises the splinting bandage against premature setting of the bandage prior to use. More particularly the invention relates to bandages in which the additive is an organic acid anhydride. The present invention also relates to a method of making a splinting bandage, to water curable prepolymers and water hardenable compositions containing the organic acid anhydride and to processes for their preparation.

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In recent years attempts have been made to make water hardenable or curable orthopaedic bandages from polymeric materials such as polyurethane and polyacrylate. Conventionally such bandages are formed from an air permeable, water permeable flexible fabric impregnated and/or coated with a reactive prepolymer system which is hardenable on exposure to water usually in the presence of a catalyst. In one type of known system the prepolymer is an isocyanate terminated prepolymer formed by the reaction of an isocyanate and a polyol. This prepolymer hardens in the presence of water and a catalyst. One problem experienced by bandages incorporating this type of prepolymer and in particular a prepolymer derived from polyethylene glycol is the somewhat short shelf life. This can be caused by the bandages being exposed to moisture or side reactions such as allophonate formation within the prepolymer in storage prior to use, whereupon the bandages will slowly harden and become useless. It is believed this can occur to such bandages in spite of carefully controlled manufacturing processes and packing in barrier packaging. It is known in the art that the storage stability of a polyurethane splinting bandage can be improved by adding a stabiliser to the bandage prepolymer to inhibit premature curing. United States

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Patent Nos. 4433680 and 4655208 disclose polyurethane splinting bandages comprising prepolymers stabilised with benzoyl chloride. It has been found, however, that benzoyl chloride is highly lachrymatory and will give the bandage an unpleasant smell. United States Patent No. 4574793 discloses polyurethane splinting bandages comprising prepolymers stabilised with methane sulphonic acid. Methane sulphonic acid, however, is a strong acid which, if mixed therewith, would breakdown the glycol components of a reaction mixture used to form polyurethane prepolymer. Such a stabiliser therefore cannot be added to the reaction mixture to stabilise the prepolymer during its preparation. Polyurethane splinting bandages with good resistance to premature setting have now been discovered which comprise a prepolymer in admixture with a stabiliser which avoids the disadvantages of the prior art stabilisers hereinabove discussed.

Accordingly the present invention comprises a water hardenable polyurethane splinting bandage comprising a flexible fabric carrying a water curable isocyanate terminated prepolymer and a catalyst therefore wherein the prepolymer is in admixture with an organic acid anhydride.

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The organic acid anhydride stabilises the prepolymer thereby inhibiting the premature setting of the bandage. It is believed that the organic acid anhydride stabilises the prepolymer by reacting with any residual or absorbed moisture or aqueous alkali component in the prepolymer which promotes the curing thereof and by forming in the presence of such components, an acidic environment which inhibits the prepolymer from curing prematurely.

Apt organic acid anhydrides are hydrocarbyl anhydrides in which the hydrocarbyl suitably contains 1 to 12 carbon atoms preferably 2 to 6 carbon atoms and may be those derived from aliphatic, alicyclic or aromatic acids which form anhydrides. Suitable anhydrides are preferably cyclic anhydrides. Favoured organic acid anhydrides include those derived from polycarboxylic acids such as aliphatic, alicyclic aromatic dibasic acids. A preferred organic acid anhydride is succinic anhydride. Such a preferred anhydride is odourless and will not discolour the first product. Less favoured organic acid anhydrides are those derived from aromatic dibasic acid such as phthallic anhydride.

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Suitably the organic acid anhydride will be present as a solid in the dry prepolymer, that is the anhydride will be insoluble in the prepolymer. Suitably the organic acid anhydride will be in finely divided form that is the particles will suitably have a diameter of less than 150 $\mu$ m, and favourably below 100 $\mu$ m. The average particle size of the anhydride is generally below 75 $\mu$ m and is preferably from 30 to 40 $\mu$ m.

Suitably the organic acid anhydride will be present in an amount of 0.1 to 5% by weight of the prepolymer, for example 0.78%, 1.0% and 1.25%. Other stabilisers may be present in the prepolymer in addition to the organic acid anhydride. An apt stabiliser is methane sulphonic acid which may be present in an amount which is 0.01 to 1.0% by weight of the prepolymer.

Suitable isocyanate terminated prepolymers for use in the splinting bandages of the present invention include those described in our United Kingdom Patent No.2092606B at page 2 line 12 to 21 and page 4 line 13 to page 10 line 13 and in our United States Patent No. 4427003.

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Other suitable isocyanate terminated prepolymers for use in the splinting bandages of the present invention include those described in Germany Offenlegungsschriften Nos. 2353212 and 2357931, and European Patent No. 0 086 621.

Highly suitable water curable prepolymers for use in the invention are derived from a polyol and an isocyanate and also contain an organic acid anhydride stabiliser.

In another aspect the invention provides a water curable isocyanate terminated prepolymer for use in a bandage of the invention in which the prepolymer is derived from a polyol and an isocyanate and contains an organic acid anhydride.

Highly suitable prepolymers for use in the splinting bandage of the present invention are derived from polyols which are polyoxyalkylene oxide adducts such as ethylene oxide adducts, propylene oxide adducts, tetramethylene oxide adducts of mixtures thereof.

Favoured prepolymers for use in the invention however comprise a polyol derived from an ethylene oxide adduct.



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The polyol will normally have a reaction functionality of two or more than two and an isocyanate which has a reaction functionality of two or more than two. The reaction functionality of the isocyanate is preferably between two and three and is most preferably two.

A preferred isocyanate terminated prepolymer is derived from an aromatic isocyanate having a reaction functionality of between 2 and 3 and a polyol mixture containing at least one diol which is preferably a polyoxyethylene diol and at least one triol.

The polyol mixture will aptly contain sufficient oxyethylene units to render the prepolymer water absorbent. Such water absorbent prepolymers advantageously lower the set times and also the surface tack of a setting bandage.

In a further aspect the present invention provides a water hardenable composition for use in a bandage of the invention which comprises and an isocyanate terminated prepolymer of the invention and a catalyst.

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Suitable catalysts for use in the water hardenable splinting bandages of the present invention include those described in United Kingdom Patent No. 2092606B at page 3 line 10 to page 4 line 11 and in United States Patent No. 4427003. Such catalysts are water soluble but insoluble in the prepolymer. Aptly the catalyst is an inorganic material which has an alkaline reaction in water. Suitably the catalyst is a solid water soluble carbonate or bicarbonate and includes alkali metal carbonates and bicarbonates. Preferred catalysts are sodium carbonate and potassium carbonate of which potassium carbonate is preferred.

Other catalysts which may be employed in the water hardenable splinting bandage of the present invention include these described in United Kingdom Patent No. 1578895 which employs amino polyols as catalysts and as the polyol components, those disclosed in International Application No. WO 81/00671 which employs dimethyl ethanolamine or a mixture of dimethyl ethanolamine and bis(2-dimethylaminoethyl) ether and those disclosed in European Patent No. 0086621 and United States Patent No. 4574793 including dimorpholino-diethylether and bis(2,6-dimethylmorpholino) diethylether catalysts.

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The amount of catalyst present in admixture with the prepolymers of the present invention will normally be from 0.1 to 40% by weight. Suitably the amount of alkali metal carbonate or bicarbonate catalyst will be 2  
5 to 20% by weight and preferably will be 3 to 10% by weight of the prepolymer, for example 4,5 or 6%. Suitably the amount of dimorpholino-diethylether or bis(2,6-dimethylmorpholino) diethylether catalyst will be 0.1 to 10% of weight and preferably 0.3 to 4% by  
10 weight of the prepolymer.

Favoured flexible fabrics for carrying the prepolymer, catalyst and anhydride in the bandages of the present invention include those described in United Kingdom Patent No. 2092606B at page 10 lines 14 to page  
15 11 line 10 and United States Patent No. 4427003 and in our copending European Patent Application No. 94222 at pages 38 and 39.

The bandages may be conventionally packaged in heat sealed polyethylene pouches such as metal foil  
20 polyethylene laminate pouches. Although such pouches are meant to exclude water and moisture vapour, it has been found difficult to ensure that moisture vapour is

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excluded from the pouches on prolonged storage and so in some instances the water-curable bandages will prematurely set. It has been found that with bandages in which the water-curable prepolymer includes an organic acid anhydride the tendency for premature setting is much reduced so giving the bandages of the invention a longer storage capability than has hitherto been available without such a stabiliser.

In use the bandages are brought into contact with water normally by immersion and are wrapped around an injured limb. The setting bandage has a working time sufficient to allow the bandage to be positioned on the affected part of the body and a set time at which the cast is rigid. The presence of the organic acid anhydride in the prepolymer allows the bandage to possess working and set times which are suitably 1 to 6 minutes and 5 to 30 minutes respectively.

The prepolymers may be prepared by the conventional methods which are described in United Kingdom Patent No. 2092606. The organic acid anhydride can be mixed with the prepolymer after preparation. It has been found, however, that prepolymers prepared using a polyethylene glycol component tend to set prematurely

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during or immediately after preparation. It is therefore preferred, when such a prepolymer is prepared, to mix the organic acid with the polyethylene glycol component prior to preparation of the prepolymer to inhibit setting of the prepolymer in the reaction container.

Thus in another aspect the invention provides a process for preparing a water curable isocyanate terminated prepolymer of the invention which comprises mixing a polyol with an organic acid anhydride and reacting the polyol with excess isocyanate.

The prepolymer can then be mixed with a catalyst to prepare a water curable hardenable composition of the invention.

Thus in a further aspect the invention provides a process for preparing a water hardenable composition of the invention which comprises mixing a catalyst with an isocyanate terminated prepolymer of the invention.

The catalyst which may be a particulate solid water soluble catalyst such as potassium carbonate or a liquid catalyst such as dimorpholino-diethylether or

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bis(2,6-dimethylmorpholino) diethylether may be mixed into the prepolymer by a conventional method.

Inert materials may be incorporated into the prepolymer mixture, if necessary, as fillers, reinforcing fillers or colouring agents.

The prepolymer mixture can then be used to prepare a bandage of the invention.

In another aspect the invention provides a method of making a water hardenable polyurethane splinting bandage of the invention which comprises coating or impregnating a flexible fabric carrier, which has apertures of sufficient size to allow water to permeate the bandage and react with the prepolymer, with a mixture of a water curable isocyanate terminated prepolymer containing an organic acid anhydride inhibitor and a catalyst.

The flexible fabric may be coated or impregnated and made into bandages by conventional methods known in the art.

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The invention will be now illustrated by references to the following examples.

EXAMPLE 1

Preparation of Prepolymer

5           The prepolymer was prepared from the following components:

Polyethylene glycol (mol wt 1000)	1 moles
Polypropylene glycol (mol wt 1025)	1.25 moles
Methylene-bis-(4 cyclohexyl-	
10       isocyanate) sufficient to give	
a mole ratio of NCO/OH of	3.75/1
Succinic anhydride	1% based on
	weight of
	components.

15           The glycols were mixed together with the finely ground succinic anhydride in a reactor which was adapted to be purged with dry nitrogen. The isocyanate was added and the reactor purged with dry nitrogen. The reaction mixture was then stirred for 90 minutes at

20       55°C. The prepolymer formed was allowed to cool and

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then discharged into a container which had previously been purged with dry nitrogen. The container was sealed until the prepolymer was required.

Preparation of Bandage

5           A portion of the prepolymer (100g) prepared above was mixed with Analar grade potassium carbonate (6g) and 0.2% antifoaming agent. This prepolymer mixture was spread onto 8cm wide 612 cotton leno gauze by a blade over flat bed coating technique as a hot melt at a  
10           temperature of approximately 60°C cotton in a closed area purged with carbon dioxide to obtain a dry atmosphere. The bandage strip had an apertured coating of prepolymer at a weight per unit area of 62gsm. The bandage strip was cut into 1 metre lengths and rolled  
15           up. The bandage rolls were then stored in heat sealed pouches of 62.5µm thick low density polyethylene which had previously been purged with nitrogen. Prepolymers containing succinic anhydride showed satisfactory ageing characteristics.

20           The bandage may be made into a cast by immersing the bandage in water and wrapping the unrolled bandage around a 2.5cm diameter spindle. The bandage will have



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working time of 5 minutes and a set time of 12 minutes. The resulting cast will be rubbery at first but will rapidly harden.

#### EXAMPLE 2

5           The prepolymer is prepared from the following components:

	Poly (oxypropylene) glycol (mol wt 1025)	44.0g
	Poly (oxypropylene) triol (mol wt 400)	31.0g
	Modified diphenylmethane	
10	diisocyanate (Isonate 143-L)	12.0g
	Dimorpholino-diethyl ether	3.4g
	Succinic anhydride	1% based on weight of components

15           The isocyanate is placed in a reactor which is purged with nitrogen. The glycols are mixed together, dried and mixed with the finely ground succinic anhydride. The polyol mixture is added to the reactor using a dropping funnel over a period of 25 to 30  
20 minutes. After the addition is complete, the reaction mixture is then stirred for 1 hour at 55°C. The

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prepolymer formed is allowed to cool, mixed with dimorpholino-diethylether and then discharged into a container which has been previously purged with dry nitrogen. The container is sealed until the prepolymer is required.

Bandages may be prepared by the method described in Example 1.

### EXAMPLE 3

The prepolymer is prepared from the following components:

Poly (oxypropylene) diol (mol wt 1025)	80g
Modified diphenyl methane diisocyanate (Isonate 143-L)	120g
N,N-dimethylethanolamine	2ml
Succinic anhydride	1% based on weight of components

The isocyanate is placed in a reactor which is fitted with a stirrer, protected from ingress of moisture and may be purged with dry nitrogen. Under an

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atmosphere of dry nitrogen a mixture of the diol, amine  
and finely divided succinic anhydride is added slowly to  
the stirred isocyanate. The temperature of the  
reaction mixture is kept below 50°C. The prepolymer  
5 formed is allowed to cool and is then discharged into a  
dry sealable container which has been previously purged  
with dry nitrogen.

Bandages may be prepared by the method described in  
Example 1.

10 EXAMPLE 4

The prepolymer is prepared from the following  
components:

	Diphenylmethane diisocyanate	50g
	Propoxylated triethanolamine	40g
15	Succinic anhydride	1.2% based on the weight of components

The prepolymer is prepared in a similar manner to  
20 that described in Example 3.

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An analogous prepolymer is prepared using phthallic anhydride.

EXAMPLE 5

A prepolymer was formed from the following components:

PEG 1000	3 moles
Poly (oxytetramethylene) glycol	
(Mol wt. 1000)	3 moles
Arcol 3130	4 moles
Isonate 143 - L	sufficient to give
	a NCO to OH ratio
	of 3.53 : 1
Succinic anhydride	1% by weight of the
	components

The prepolymer of this example was prepared in the same manner as example 1, the finely ground succinic anhydride being mixed with the PEG 1000 prior to being mixed with the other polyols. PEG 1000 is a polyoxyethylene glycol with an average molecular weight of approximately 1000 available from B.P. Chemicals.

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Arcol 3130 is a polyoxypropylene triol with an average molecular weight of approximately 400 available from Arco Chemicals.

5 Isonate 143 - L is a diphenylmethane - 4,4' - diisocyanate containing polycarboniimide adducts available from Dow Chemicals.

10 A bandage, using the prepolymer prepared above, was prepared in the same manner as Example 1 except that the amount of potassium carbonate mixed with the prepolymer was 3% by wt. and the prepolymer mixture was coated by means of nip rollers at 22°C on to a flexible knitted glass fibre substrate (length 350 cm, width 7.5 cm) at a weight per unit area of 25 g/m<sup>2</sup>.

15 The bandage rolls were stored in individual heat sealed polyethylene coated aluminium foil pouches, which had been previously purged with nitrogen.

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EXAMPLE 6

A prepolymer was prepared in the same manner as Example 5 using the following components:

5	P E G 1000	6 moles
	Arcol 3150	4 moles
	Isonate 143 - L	sufficient to give a
		NCO to OH ratio of
		3.53 : 1
10	Succinic anhydride	1% by weight of the
		components.

Analogous prepolymers were prepared using phthallic anhydride.

Bandages containing the prepolymers were prepared and stored in the same manner as Example 5.

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EXAMPLE 7

A prepolymer was prepared in the same manner as Example 5 using the following components:

	P E G	1000	3 moles
5	PPG	1025	3 moles
	Arcol	3150	4 moles
	Isonate 143 - L		sufficient to give a NCO to OH ratio of 3.53 : 1
10	Succinic anhydride		1% by weight of components.

PPG 1025 is a polyoxypropylene glycol having an average molecular weight of approximately 1025, available from B.P. Chemicals.

15 Bandages containing the prepolymer mixed with 6% by weight of potassium carbonate were prepared and stored in the same manner as Example 5.

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EXAMPLE 8

A prepolymer was prepared from the following ingredients:

	P E G	1000	6 moles
5	Arcol	3150	4 moles
	Isonate 143 - L		sufficient to give a
			NCO to OH ratio of
			3.53 : 1
	Succinic anhydride		1% be weight
10	Methane Sulphonic Acid		0.03% of components
	Antifoam		0.3% by weight.

The prepolymer was prepared in the same manner as Example 5, the antifoam being mixed with the polyol components and the methane sulphonic acid being added to the prepolymer after it had been prepared.

Bandages, containing the prepolymer, were prepared and stored in the same manner as Example 5 except that the prepolymer contained 0.55% by weight of catalyst bis(2,6 - dimethylmorpholino) diethylether instead of potassium carbonate.



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The bandages of Examples 5 to 8 on initial storage did not exhibit premature setting. In addition the bandages of Example 7 were found to be satisfactory after being stored for 6 months under accelerated ageing conditions at a temperature of 40°C.

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The bandages of these samples before and after storage were found to have satisfactory working and set times when used to form a cast.

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CLAIMS

1. A water hardenable polyurethane splinting bandage comprising a flexible fabric carrying a water curable isocyanate terminated prepolymer and a catalyst  
5 therefor wherein the prepolymer is in admixture with an organic acid anhydride.
2. A bandage as claimed in claim 1 in which the anhydride is an aliphatic dibasic acid anhydride.
3. A bandage as claimed in claim 2 in which the  
10 anhydride is succinic anhydride.
4. A bandage as claimed in any of claims 1 to 3 in which the anhydride is in particulate form and is present as 0.5% to 1.5% by weight of the prepolymer.
5. A water curable isocyanate terminated prepolymer  
15 for use in a bandage of any of claims 1 to 4 in which the prepolymer is derived from a polyol and an isocyanate and contains an organic acid anhydride.
6. A prepolymer as claimed in claim 5 in which the anhydride is succinic anhydride.

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7. A prepolymer is claimed in either claims 5 or 6 in which polyol is an ethylene oxide adduct and the isocyanate is an aromatic isocyanate.

8. A prepolymer as claimed in any of claims 5 to 7 in  
5 which the polyol is a propylene oxide adduct.

9. A water hardenable composition for use in a bandage of any of claims 1 to 4 which comprises a prepolymer of any of claims 5 to 8 and a catalyst.

10. A composition as claimed in claim 9 in which the  
10 catalyst is potassium carbonate.

11. A composition as claimed in claim 9 in which the catalyst is dimorpholino diethylether.

12. A composition as claimed in claim 9 in which the catalyst is bis(2,6-dimethyl morpholino) diethylether.

15 13. A method of making a water hardenable splinting bandage as claimed in any of claims 1 to 4 which comprises coating or impregnating a flexible fabric carrier, which has apertures of sufficient size to permeate the bandage and react with the prepolymer, with

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a mixture of water curable isocyanate terminated prepolymer containing an organic acid anhydride inhibitor and a catalyst.

14. A process for preparing a water curable isocyanate terminated prepolymer as claimed in any of claims 5 to 8 which comprises mixing a polyol with an organic acid anhydride and reacting the polyol with excess isocyanate.

15. A process for preparing a water hardenable composition as claimed in any of claims 9 to 11 which comprises mixing a catalyst with an isocyanate terminated prepolymer as claimed in any of claims 5 to 8.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00716

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> :     A 61 L 15/07		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	A 61 L 15/07	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	FR, A, 1449774 (EASTMAN KODAK) 19 August 1966 see page 9, right-hand column	1-15
Y	EP, A, 0086621 (JOHNSON & JOHNSON) 24 August 1983 see claims 1-6 cited in the application	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> * Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11th January 1988	17 FEB 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN	

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

GB 8700716  
SA 19002

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/02/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE-A- 1570513	31-07-69
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